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CALCIUM CHLORIDE

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By Paul M. Tyler 2/

INTRODUCTION

Calcium chloride is a conspicuous example of a former waste product that has found a place for itself in the onward march of civilization. Formerly considered a troublesome constituent of the effluent sewage of many chemical manufacturing plants and salt works, it has now become a commercial product of substantial importance, with sales aggregating almost six million dollars in 1929.

The point has not yet been reached where it would seem profitable to undertake large-scale production of calcium chloride as a main product, but as a byproduct it has become an item that warrants serious consideration by all who are in a position to recover it at sufficiently low cost. The largely increased demand for bromine and for certain magnesium salts, which are likewise potential byproducts associated with calcium chloride in most salt-works bitterns (and brines generally), adds further impetus to commercial research directed toward the fuller utilization of the natural saline resources of the United States.

DESCRIPTION AND PROPERTIES

Calcium chloride ($CaCl_2$) is a white, highly deliquescent salt. It is marketed in three forms: (1) Fused or anhydrous; (2) hydrated ($CaCl_2.6H_2O$), containing 49 percent of water of crystallization; and (3) partly dehydrated ($CaCl_2.H_2O$), containing theoretically about 14 percent of water. The fused salt is available in C.P., U.S.P., and technical grades. The partly dehydrated form is available as solid (73-75 percent), powder (77-80 percent), and flake (77 to 80 percent). The solid is packed in drums containing 650 to 665 pounds; the powder and the flake are both sold in 400-pound drums; and flake is also available in 100-pound bags. The hydrated salt, with 6 molecules of water, is the one which crystallizes in transparent hexagonal prisms when a solution is evaporated, but even it quickly takes on water; and

1/ The Bureau of Mines will welcome reprinting of this article, provided the following footnote acknowledgment is used: "Reprinted from U. S. Bureau of Mines Information Circular 6781."

2/ Chief engineer, Rare Metals and Nonmetals Division, U. S. Bureau of Mines, assisted by E. P. Youngman. Domestic production statistics compiled from reports by A. T. Coons, Mineral Statistics Division.

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since it contains scarcely 50 percent of the dry salt, it is rather uncommon on the market. A liquid product containing 38.6 percent $CaCl_2$, however, is sold in tank-car lots.

Upon evaporation from solution, $CaCl_2.6H_2O$ forms in transparent hexagonal prisms which melt at 29° C. The first 4 molecules of water are readily removed, but the other 2 are not driven off below 200° C. The anhydrous salt fuses at around 800° C.

Calcium chloride unites not only with water but also with ammonia (forming $CaCl_2.8NH_3$) and alcohol. When the anhydrous salt unites with water considerable heat is liberated, but when the crystalline hexahydrate ($CaCl_2.6H_2O$) dissolves in water a strong cooling effect is produced; when it is mixed with snow, in the same manner as common salt is mixed with ice in making ice cream, temperatures considerably below the freezing point of mercury or around -55° C. can be obtained.

The following suggestions with regard to commercial purchases are quoted from an article in a British trade journal:3/

> For general engineering shop purposes, as in drying ovens and spray-equipment driers, calcium chloride is purchased in airtight containers, usually of tinned or galvanized iron with lever-lid covers of 14 pounds to 112 pounds capacity; the smaller sizes are strongly advocated where requirements are small. Lump size averages from 1 to 2 inches linear dimension, although for bigger plant installations, larger pieces can be efficiently employed. Smaller particles, say ¼ inch and downward, and dust need to be maintained at a minimum, as they appreciably add resistance to flow, cause clogging and early exhaustion of the charge from excessively unequal deliquescence.
>
> The initial water content is naturally of importance; 4.0 percent to 5.0 percent is the amount commonly encountered, although material as low as 2½ percent is not unusual. A maximum limit of 5.0 percent is quite acceptable when it is remembered that in many applications calcium chloride is not scrapped until it has absorbed more than its own weight of water. These water figures are based on a method of determination standardized to the following conditions: The sample representative of the bulk is transferred to a mortar, previously warmed to about 70° C., and rapidly crushed to a fairly fine degree. From a weighing bottle about 5 grams are weighed into a covered crucible, heated gradually till fusion commences, and then cooled in a desiccator and reweighed. Reheating to constant weight is resorted to if necessary. The loss in weight expressed as a percentage is reported as water content.

* * * *

3/ Chemical Trade Journal (London), "Arma," Calcium Chloride: Quality Requirements for Industrial Air Drying: Vol. 90, no. 2351, June 10, 1932, p. 567.

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In conclusion, it may be summarized that the essential features to be watched in selecting a suitable commercial calcium chloride are: (1) Water content; (2) physical form--porous, unfused type; and (3) size, limiting the maximum small material to, say, 5 percent, passing through $\frac{1}{4}$-inch mesh, and stating the mesh through which the remainder must pass.

USES

The principal use of calcium chloride, accounting for probably more than half the total consumption, is for laying dust on dirt roads. It is used extensively also in refrigerating systems and as a curing and hardening agent in concrete. A more complete list of uses as given in the Condensed Chemical Dictionary (1930 edition) is as follows:

> Dehydrating agent; food preservative; road dressing, fireproofing paints; freezing mixtures and solutions; sizing compounds; mineral waters; chemical (ammonium chloride, precipitated chalk, tartaric acid, drying gases); gunpowder; wood preservatives; hydraulic pressure solutions; metallic calcium; automobile antifreeze; fire bucket and automatic sprinkler solutions; dry colors; dehydrating petroleum distillates; pharmaceutical preparations; water purification.

In addition, it has been employed as a coal-dusting agent, an agent in the production of a high boiling point, a liquid in traps for plumbing systems, and in the preparation of wall plaster.

The industries in which it is used in England, according to the London Chemical Age Year Book, 1932, are: Brewing, cotton, explosives, mineral waters, paints, paper, starch, and tartaric acid.

Notes on certain specialized uses follow:

Freezing Mixtures

The crude fused product (obtained from Solvay soda works) is generally used in the artificial ice factories in the form of a 6 to 10 percent solution of $CaCl_2$ as a cooling brine, as this solution does not freeze even at 8 to 9° below zero. This crude product contains 70 to 75 percent of $CaCl_2$.

Hardening and Curing of Cement and Concrete

With respect to the use of calcium chloride in concrete, the research methods employed and the conclusions reached by the laboratory maintained by the American Portland Cement Association and the Lewis Institute, Chicago, are briefed in an article appearing in the Chemical Trade Journal and Chemical Engineer.[4/] The use of chemical compounds for hastening the hardening of

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4/ Abrams, Duff A., Calcium Chloride in Concrete; Recent American Research: Chem. Trade Jour. and Chem. Eng., vol. 76, no. 1968, Feb. 6, 1925, pp. 166-167.

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Portland cement concrete had aroused great interest in the United States and in Great Britain, and experience and tests had shown that calcium chloride, or materials having this compound as a principal constituent, were probably the most promising. The laboratory made 7,500 strength tests of concrete and mortar at ages ranging from two days to three years. The most important conclusion, as summarized in the article referred to, is the following:

> In the use of calcium chloride no advantage was gained for percentages of the commercial product greater than 2 or 3 percent of the weight of cement (chlorine content, 1 to 1½ percent). This amount when used in mixes of about 1:5 and in consistencies suitable for building construction showed an increase in compressive strength of from 100 pounds to 200 pounds per square inches, which increase was practically constant at ages of 2 days to 3 years. For richer mixes and drier consistencies, the strength increase was greater and for leaner mixes and wetter concretes it was less.

Fire Buckets, et Cetera

Calcium chloride in fire buckets has the advantage over water in that it does not corrode metal, has a lower freezing point, and because of its affinity for water tends to keep the buckets full by extracting moisture from the air.

Coal Dusting

A national conference on weights and measures at the Bureau of Standards discussed the comparatively new development of treating coal chemically. The benefits claimed are the following:5/ (1) Coal so treated remains free from flying dust for at least 1 year; (2) the treatment reduces smoke, and the coal tends to burn cleaner and brighter; and (3) the treatment tends to reduce slack and to seal moisture in the pores of the coal to some extent.

With respect to the efficiency of calcium chloride in allaying coal dust in mines (as a substitute for rock dusting), the Bureau of Mines has made investigations that prove that it does not accomplish the desired purpose. According to George S. Rice, chief mining engineer of the bureau, one of the serious objections to using it is that it creates a false sense of security because of the packing down of the road material after its use. Many tons of coal dust accumulate each day in a large coal mine, and several tons are distributed through the haulageways, and the fresh dust resting on the hardened floor is raised into the air easily by an initial explosion of any kind. Any system of keeping the dust moist by the use of deliquescent salts, as also in fact by straight watering, is an impossibility from the standpoint of efficiency.

5/ Special to the Journal of Commerce, June 8, 1930.

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Industrial Air Drying[6]

Calcium chloride is one of the important materials, perhaps the most popular, employed where air supplies need to be dried for use in various parts of a factory and it is convenient and economical to install self-contained drying units on the site of each application, so that air passes directly from the drier to the job. Its advantages for such a purpose have been summarized as follows:

> Apart from its desiccating qualities, it is convenient and safe to handle and store, is nonvolatile, relatively noncorrosive, and it can be purchased quite cheaply. It is the best material to employ in the electrical industries, in which not only is it largely employed in connection with air supplies for paint, enamel, and lacquer spraying, but also for desiccating equipment in which atmospheres reasonably free from moisture are desired for temporarily storing apparatus such as coils or mica and paper condensers at intermediate stages of manufacture. In simply designed fixtures calcium chloride may be contained without any risk of contaminating the work itself. Other drying agents, such as sulphuric acid or phosphorus pentoxide, do not afford the same extent of convenience for efficient distribution with an equal degree of safety and compactness.

Reactivation by Heating

In many instances it pays to reactivate calcium chloride by heating for reuse. The water content should not be allowed to rise to too high a level before this recovery is effected; and heating should be gradual if fusion, due to the presence of hydrates, is to be avoided.

> A final temperature of 400°-500° C. is recommended. In the majority of instances, however, it is more economic to allow the charge to become fully exhausted, and then to run it to waste. Such is the usual practice in relation to air driers for spray pistols. Here it is best to run a battery of two units in series. They consist of iron cylinders loaded with calcium chloride, separated by a number of horizontal perforated plates. Air enters near the bottom and leaves at the top; a sump provides for the draining down of liquid that can be drawn off. Periodically, when one cylinder is recharged the air flow is reversed through the battery, so that outgoing air is always last in contact with fresh drying agent.[7]

SOURCES

In the United States, calcium chloride is produced commercially (1) as a byproduct in the Solvay process for the manufacture of sodium carbonate, and (2) as a joint product from natural salt brines from which bromine also is

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6/ Chemical Trade Journal (London), Work cited.
7/ Chemical Trade Journal (London), Work cited.

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generally recovered. In Germany it is produced from carnallite in the Stassfurt potash deposits and also as a byproduct of the Solvay process.

A few minerals contain calcium chloride (usually in conjunction with magnesium chloride and alkaline chlorides), notably tachydrite, which contains 21 percent $CaCl_2$ and 36 percent $MgCl_2$, and carnallite, which contains 3 percent $CaCl_2$ and 31 percent $MgCl_2$--both of which are found in the Stassfurt beds. Calcium chloride is an almost universal constituent of spring and river waters and of sea water. The mother liquors of salt works contain large percentages of the compound.

The origin of calcium chloride waters is discussed briefly in the next section of this paper, but with respect to the general subject of calcium chloride occurrences the reader is referred to the publications listed below.

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LANE, A. C. Michigan iron mines and their mine waters. Jour. Canadian Min. Inst., vol. 12, 1909, pp. 114-129.

LANE, A. C. Mine Waters. Proc. Lake Superior Min. Inst., vol. 13, 1908, pp. 63 ff.

MILLS, R. VAN A., and WELLS, R. C. The evaporation and concentration of waters associated with petroleum and natural gas. U. S. Geol. Survey Bull. 693, 1919, 100 pp.

PALMER, CHASE. Geochemical interpretation of water analyses. U. S. Geol. Survey Bull. 479, 1911, 31 pp.

PHALEN, W. C. Salt resources of the United States. U. S. Geol. Survey Bull. 669, 1919, 277 pp.

RICHARDSON, G. B. Note on Appalachian oil-field brines. Econ. Geol., vol. 12, No. 1, Jan., 1917, pp. 39-41.

ROGERS, G. S. The Sunset-Midway oil field, Calif.; pt. 2, Geochemical relations of the oil, gas, and water. U. S. Geol. Survey Prof. Paper 117, 1919, 100 pp.

WASHBURNE, C. W. Chlorides in oil-field waters. Trans. Am. Inst. Min. Eng., vol. 48, 1915, pp. 687-693.

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ORIGIN OF CALCIUM CHLORIDE WATERS[8]

A search of geologic literature shows that papers dealing with calcium chloride brines and their origin are far from numerous. However, several contributions have been made to this subject during the past 50 years, and the various ideas that have been advanced will be reviewed briefly.

Although calcium chloride waters occur in various parts of the world they are far from a common type of oil-field brine and therefore seem to owe their origin to certain special conditions.

In 1875 T. Sterry Hunt[9] advanced the idea that the deep-seated calcium chloride waters of Ontario are long-buried bitterns derived by evaporation from the waters of ancient seas in which calcium was more abundant than in the present-day ocean. This theory was supported by A. C. Lane,[10] who considered the highly concentrated Huronian brines high in calcium chloride, which are found in many of the Michigan iron and copper mines, to be bitterns derived from a primordial sea water that was a weak solution of calcium and other chlorides.

This theory of primordial calcium chloride sea water has nothing to commend it, as (1) it is difficult to see how life could have existed in marine waters of this character, and (2) it does not adequately explain the numerous other occurrences of calcium chloride waters having a rather wide geologic range. It can be dismissed as a possible explanation of the calcium chloride waters under consideration, as it is fairly certain that the composition of the ocean in Tertiary time was not essentially different from that at present. Furthermore, the Sespe beds in which Ventura County calcium chloride waters occur are not marine, but continental.

Later C. W. Washburne[11] advanced the theory that calcium, magnesium, and sodium chlorides may have been introduced into underground brines by emanations from deep-seated basic magmas. If this were true, the composition of the deeper underground waters should be essentially the same in any one province, irrespective of the beds in which they are found. That this is not the case is clearly shown in many places, notably in Ventura County, where the calcium chloride waters from the South Mountain and Shiells' Canyon fields differ widely from the modified connate sea waters found in the Ventura Avenue field not far distant.

8/ Hudson, F. S., and Taliaferro, N. L., Calcium Chloride Waters from Certain Oil Fields in Ventura County, Calif.: Bull. Am. Assoc. Petrol. Geol., vol. 9, no. 7, October, 1925, pp. 1081-1082.

9/ Chemical and Geological Essays, Boston, 1875, p. 117.

10/ Lane, A. C., Mine Waters: Proc. Lake Superior Min. Inst., vol. 13, 1908, pp. 63 ff.; and Michigan Iron Mines and their Mine Waters: Jour. Canadian Min. Inst., vol. 12, 1909, pp. 114 ff.

11/ Washburne, C. W., Chlorides in Oil-Field Waters: Trans. Am. Inst. Min. Eng., vol. 48, 1915, pp. 687-693.

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The most thorough work on the subject is by Mills and Wells,[12] who explain the high chlorine content and very high concentration of certain Appalachian oil-field brines as due to changes in the waters after their inclusion in the sediments. These changes are supposedly due to solution of certain rock constituents, to organochemical processes, to chemical reactions brought about by the mixing of waters, to reactions due to heat, to reactions between dissolved constituents of the waters and certain constituents of the rocks, and, most important, in their opinion, to changes and concentration brought about by the drying effect of escaping gases. However applicable this theory of the concentration and modification of the waters by escaping gases may be to the Appalachian waters, it does not seem to apply to the calcium chloride waters of Ventura County (Calif.), as the latter are of comparatively low concentration. . . .

The accompanying table shows analyses of various types of chloride waters.

12/ Mills, R. van A., and Wells, R. C., The Evaporation and Concentration of Waters Associated with Petroleum and Natural Gas: U. S. Geol. Survey Bull. 693, 1919, 100 pp.

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TABLE 1. - Comparison of various types of chloride waters[a] I.C. 6781

Salt	Ocean water		Artificial Bitterns derived from ocean water		Natural bitterns			Mine waters			Oil- and gas-well waters: Appalachian			Oklahoma		Texas	California: South Mountain Field			California: Wiley Canyon
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Ca	1.20	1.18	0.26	.....	4.37	2.01	.10	17.49	30.78	20.56	10.85	14.68	10.90	9.76	6.27	10.89	18.52	27.46	20.09	19.89
Mg	3.71	3.59	3.72	10.05	13.62	11.13	17.55	1.21	0.01	6.82	.94	.65	.95	.74	1.53	.93	.63	tr.	tr.	.25
Na	30.54	31.08	32.06	20.39	13.55	19.90	11.27	18.36	5.63	7.57	24.51	21.01	25.32	27.57	29.38	22.20	18.10	9.43	17.38	16.92
K	1.11	.71	.78	2.25	.....	.....	.....	.67	.....	tr.	1.97	1.41	.67	tr.	.77	2.81	.....	.....	.....	.....
CO_3	.05	.18	.....	.....	tr.	.....	.04	.43	.01	.....	.....	.....	.....	.....	.....	.....	.....	1.80	.50	.75
HCO_3	.31	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.74
SO_4	7.63	7.72	5.78	14.64	.23	.....	6.82	.13	.01	5.42	.02	.40	.17	.74	tr.	16.44	.....	.22	.15	1.32
Cl	55.21	54.32	56.18	49.99	68.15	66.96	64.22	61.66	63.56	59.63	61.42	60.95	61.44	61.19	61.74	46.73	62.75	61.09	61.83	60.13
Br,I	.19	1.15	1.22	2.68	.....	.....	.....	.....	.....	.....	.26	.90	.55	tr.	.31	.....	.....	.....	.....	.....
Total	100.00	100.00	100.00	100.00	99.97	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Total dissolved solids (grams per liter)	34.0-38.33	38.63	33.31	26.12	33.02	30.12	26.02	36.02	12.32	?	19.35	26.6	19.7	35.3	30.7	03.39	30.10	27.80	31.25	27.08

a F. S. Hudson and N. L. Taliaferro. b Includes 1.31 strontium. c Parts per thousand. 1/ Mean of 77 analyses of ocean water, collected by Challenger expedition, W. Dittmar, analyst. Analysis recast by R. C. Wells, U.S.G.S. Prof. Paper 120-A (1918), p.15. 2/ Mediterranean water, J. Usiglio, analyst. Recast by F. W. Clarke, U.S.G.S. Bull.216 (1916), p.219. 3/ Mediterranean water, concentrated from density 1.0258 to 1.21. Reference same as 2. 4/ Mediterranean water, concentrated from density 1.0258 to 1.264. Reference same as 2. 5/ Dead Sea, Palestine, F. W. Clarke, U.S.G.S. Bull.616 (1915), p.174. 6/ Red Lake, Crimea; same reference as 5. 7/ Elton Lake, Russia; same reference as 5. 8/ Silver Islet Mine, Lake Superior, F. D. Adams, analyst. Ann. Report. G.S. Canada, new series, vol. 1 (1885), p.17M. 9/ Quincy Mine, Hancock, Mich., G. Steiger, analyst. F. W. Clarke, U.S.G.S. Bull.616 (1916), p.185. 10/ Germania Mine, Hurley, Mich. From vug on ninth level. A. C. Lane, Jour. Canadian Min. Inst., vol. 12 (1909), p.114. 11/ Washington County (Pa.) gas well 8 miles southwest of Imperial. Brine from 6,300 feet depth, from early Devonian sandstone, George Steiger, analyst. U.S.G.S. Water Supply Paper 364 (1914), p.9. 12/ Vinton County, Ohio, Southern Oil Co., well 2,100 feet depth, J. A. Cullen, analyst. W. C. Phalen, U.S.G.S. Bull. 669, p.232. 13/ Harrison County, W. Va., South Penn Oil Co., 50-foot water sand at 2,094 feet depth, J. A. Cullen, analyst. W. C. Phalen, work cited, p.231. 14/ Tulsa County (Okla.) oil well, depth 1,148 feet, in Cherokee formation of Pennsylvanian age, R. F. Gardiner, analyst. W. C. Phalen, work cited, p.238. 15/ Tulsa County (Okla.) oil well, depth 1,173 feet, Cherokee formation, J. A. Cullen, analyst. Reference same as 14. 16/ Spur, Texas, well in Cisco formation, probably from 2,200 feet depth (Cisco is marine Pennsylvania), S. H. Warrell, analyst. J. A. Udden, Texas Univ. Bull. 28, Sci. Ser., pp. 82-89. 17/ South Mountain oil field, Ventura County, Calif. Brine from Harvey well No. 8, depth 2,037 feet, M. T. Kendall, analyst. 18/ South Mountain oil field, Ventura County, California. Brine from Willard well no. 6, depth 3,672 feet, M. T. Kendall, analyst. 19/ South Mountain oil field, Ventura County, Calif. Brine from Geo. Richardson well no. 2, depth 4,712 feet, M. T. Kendall, analyst. 20/ Wiley Canyon, Ventura County, Calif. Brine from V. R. well no. 2, depth 3,800 feet, M. T. Kendall, analyst.

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EXTRACTION

In the manufacture of soda by the Solvay process, ammonia has to be recovered from the waste liquors and returned to the process. This is accomplished by adding lime. The calcium chloride thus formed may be obtained by evaporating the waste liquors.

The recovery of calcium chloride from natural brines is essentially similar. After sodium chloride (common salt) and the bromine (if that is recovered) are removed the bittern is treated with milk of lime (or magnesium hydrate), allowed to settle, and then evaporated further to a thick syrup, which is run into metal drums before it solidifies. The liquid may alternatively be run in a viscous condition onto floors over which cold water is circulated in pipes; the sudden solidification produces a tension in the solidified product enabling it to be broken easily by sledgehammers. It is passed through a rotary crusher, sized, and barreled for the trade. The methods in use in Ohio and West Virginia and at certain plants in Michigan are described by Phalen, and descriptions of special processes are given in other publications listed in the footnote references.13/

The operations of the Dow Chemical Co. of Midland, Mich., are described in a popular way in Fortune.14/ This company occupies a prominent position in the production of calcium chloride, caustic soda, and chlorine and is the leading producer of bromine and magnesium products in the United States. Pertinent facts with respect to calcium chloride recovery by this company are contained in a description of its magnesium operations:15/

> A natural brine is pumped from wells 1,200 to 1,400 feet deep. It contains approximately 14 percent sodium chloride, 9 percent calcium chloride, 3 percent magnesium chloride, and 0.15 percent bromine.

13/ Phalen, W. C., Technology of Salt Making in the United States: Bull. 146, Bureau of Mines, 1917, pp. 95-7.
Smith, Otto M., Salt, a Byproduct of Condenser Cooling: Ind. and Eng. Chem., vol. 24, no. 5, May 1932, pp. 547-548.
Collings, W. R., and Shafer, J. J., (Assrs. to Dow Chem. Co.), Manufacture of Calcium-Magnesium Chloride: U. S. Patent 1,796,885-6, Mar. 17, 1931 (cf. U. S. Patnet 1,738,492).
Smith, A. K., and Prutton, Carl F. (Assrs. to Dow Chem. Co.), Method of Separating Calcium and Magnesium Chlorides: U. S. Patent 1,780,098; Chem. and Met. Eng., vol. 37, no. 11, November 1930, p. 707.
Richardson, B. P., Protecting Calcium Chloride or Other Granular Substances from Deterioration: U. S. Patent 1,692,996, Nov. 27, 1928; Chem. Abs., vol. 23, no. 3, Feb. 10, 1929, p. 676.

14/ Fortune, Dow Chemical: Vol. 3, no. 4, April 1931, pp. 58-63.

15/ Gann, John A., The Magnesium Industry: Ind. and Eng. Chem., vol. 22, no. 7, July 1, 1930, pp. 694-700.

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After the bromine is removed, the brine is treated with a magnesium hydrate slurry to precipitate the iron and other impurities, which are separated in continuous thickeners and sedimentation tanks. The decanted liquor is then evaporated until the sodium chloride has crystallized. Exhaust steam from the power plants is used for this purpose. The salt is removed on rotary filters and used for the production of chlorine and caustic soda, which in turn are consumed in the production of more valuable chemicals.

The magnesium and calcium chlorides in the rotary-filter mother liquor are separated from each other by fractional crystallization. This is made possible by the fact that, under properly controlled composition and temperature conditions, the crystals separating from a complex salt solution may have a different composition from the solids remaining in the mother liquor. In practice, this is accomplished by concentrating a solution with a 1:3 weight ratio of magnesium chloride to calcium chloride, whereupon crystals of the double salt tachydrite are formed. The composition of this salt is represented by the formula $2MgCl_2.CaCl_2.12H_2O$. It has a 2:1 ratio of $MgCl_2$ to $CaCl_2$, but its crystals are in equilibrium with a mother liquor having a $MgCl_2$ to $CaCl_2$ ratio of 1:10. The crystals and liquor are separated in false-bottom tanks. This $CaCl_2$-rich solution and wash water from the tachydrite are reworked elsewhere to give calcium chloride and Epsom salts. The tachydrite crystals are then dissolved in hot water, and the solution is transferred to a series of crystallizers, where substantially pure $MgCl_2.6H_2O$ separates, leaving a mother liquor containing $MgCl_2$ and $CaCl_2$ in a ratio of approximately 1:1. This solution, together with the $MgCl_2.6H_2O$ wash water, contains approximately half of the magnesium chloride originally present in the brine and is returned to the process for reworking as indicated in the flow sheet.

PRODUCTION

The domestic production of calcium chloride almost trebled in value and more than trebled in quantity between 1923 and 1929, amounting in the latter year to 277,010 short tons valued at $5,947,281. Available figures for total output, including the production from Solvay-process chemical plants, are as follows:

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Production of calcium chloride in the United States from all sources, 1921-1931.
(From U.S. Bureau of Census)

Year	Number of establishments	Short tons	Value	Average selling price per ton
1921	19	79,014	$2,027,385	$25.67
1923	13	90,750	2,038,632	22.46
1925	16	170,773	3,717,456	21.77
1927	15	191,123	4,442,876	23.25
1929	18	277,010	5,947,281	21.47
1931	14	232,057	4,725,085	20.36

From 1923 to 1929 the proportion of the total output derived from natural brines or salt works bitterns ranged from 40 to 50 percent; in 1921, however, it was only 30 percent of the total. Actually the chlorine in the calcium chloride produced at Solvay-process plants is a constituent of the brines pumped from wells that furnish the salt (sodium chloride) for soda manufacture at these plants, but the calcium is derived from limestone. For this reason the production from such chemical plants is not included in the statistics of production from natural brines.

Calcium (calcium-magnesium) chloride from natural brines sold by producers in the United States, 1910-1932
(From Mineral Resources of the United States, pt. 2, annual, 1910-31; Minerals Yearbook, 1932)

Year	Short tons	Value	Average selling price per ton	Year	Short tons	Value	Average selling price per ton
1910	10,971	$ 74,713	$ 6.81	1921	23,672	$ 510,723	$21.57
1911	14,606	91,215	6.25	1922	33,067	571,326	17.28
1912	18,550	117,272	6.32	1923	44,961	663,384	14.75
1913	19,611	130,030	6.63	1924	58,791	1,164,848	19.81
1914	19,403	121,766	6.28	1925	67,870	1,386,639	20.43
1915	20,535	130,830	6.37	1926	82,340	1,710,405	20.77
1916	27,709	224,997	8.12	1927	95,721	1,947,796	20.35
1917	30,503	451,480	14.80	1928	102,090	1,995,603	19.55
1918	26,624	503,452	18.91	1929	114,240	2,097,061	18.36
1919	26,123	321,596	12.31	1930	116,160	2,207,800	19.01
1920	27,849	639,471	22.96	1931	86,156	1,687,166	19.58
				1932	66,286	1,163,385	17.55

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IMPORTS

The imports of calcium chloride are mainly from Germany. Although they have increased more or less in proportion to the increase in domestic output, the quantity constitutes under 5 percent of the apparent consumption in the United States. Before 1922 import figures were not separated, except for 1910, when approximately 250 tons were reported from Germany, and in 1914, when 6,516 pounds of crude, 10,860 pounds of the pure exsiccated product and 500 pounds of the pure fused chloride came from Germany.16/ Available statistics are as follows:

Calcium chloride imported for consumption in the United States, September 22, 1922, to December 31, 1933 1/

Year	Short tons	Value	Year	Short tons	Value
1922 (Sept. 22 to Dec. 31)	740	$ 8,563	1928	9,263	$100,223
1923	3,232	48,527	1929	8,236	113,573
1924	3,996	54,542	1930	6,641	95,921
1925	2,253	37,121	1931	4,916	74,546
1926	7,372	96,742	1932	3,569	48,865
1927	6,514	85,456	1933	3,583	48,115

1/ Compiled from records of the Bureau of Foreign and Domestic Commerce by J. A. Dorsey of the Bureau of Mines.

TARIFF

Before the passage of the tariff act of 1913, calcium chloride was not specifically mentioned but was dutiable as a chemical compound or salt at 25 percent under the act of 1909.17/ It was placed on the free list by the Tariff Act of 1913 and has subsequently remained free of duty under the Acts of 1922 and 1930.

EXPORTS

Exports of calcium chloride were not separately recorded until 1929. Exports since that time are as follows: 15,425 short tons, valued at $362,658, in 1929; 21,350 short tons, valued at $513,577, in 1930; 24,351 short tons, valued at $566,573, in 1931; 17,747 short tons, valued at $378,130 in 1932, and 15,685 short tons valued at $311,821 in 1933.18/

16/ U. S. Tariff Commission, Information Survey: FL - 8, 1921, p. 31.
17/ U. S. Tariff Commission, Calcium Chloride: Tariff Infor. Surveys on the articles in par. 418 to 428, inc., of the Tariff Act of 1913, 1921, p. 31.
18/ Compiled from records of the Bureau of Foreign and Domestic Commerce by J. A. Dorsey of the Bureau of Mines.

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PRICES

As it is essentially a byproduct, calcium chloride is one of the cheaper chemicals. For some years before 1916 the price of the crude substance remained fairly constant at about $13 a ton, but in the latter part of that year it rose rapidly to more than double this figure. Prices for specified years, as reported by the Oil, Paint, and Drug Reporter, are recorded in the accompanying tables. Attention is also called to the table on page 13, which gives the average prices actually received by producers f.o.b. works, as reported to the Bureau of Mines. These figures, it will be noted, are much lower than the trade-journal quotations for earlier years but are in fairly close agreement after 1916, except for a period between 1919 and 1925. During certain years it is possible that a larger proportion of the domestic product was marketed as a liquid at a correspondingly low price. Recent quotations for imported calcium chloride are nominally higher than those for domestic grades, but this may be due in part to the fact that they are offered f.o.b. New York, whereas domestic prices are f.o.b. works. In earlier years, however, the imported material was quoted uniformly at higher prices than the domestic.

Average wholesale prices of calcium chloride, New York, spot market, per short ton, 1913-1923
(From Oil, Paint, and Drug Reporter)

Year	Value	Year	Value
1913	$13.00 - $18.00	1918	$21.00 - $24.00
1914	13.00 - 16.00	1919	18.00 - 25.00
1915	11.70	1920	19.00 - 33.00
1916	11.70 - 21.00	1921	25.00 - 38.00
1917	23.00 - 30.00	1922	24.00 - 32.00

Prices of calcium chloride, per short ton, 1923-1933
(From Oil, Paint, and Drug Reporter)

Year	Domestic (f.o.b. works)		Imported (c.i.f. New York)
	Solid	Flake	Solid
1923	$24.00	$30.50	$20.50
1924	24.00	30.00	18.00 - 24.00
1925	21.00	27.00	19.00 - 20.00
1926	21.00	27.00	19.00 - 20.00
1927	21.00	27.00	19.00 - 19.50
1928 1/	20.00	25.00	18.50 - 20.00
1929 2/	20.00	22.75	17.50 - 19.00
1930	20.00	22.75	18.00 - 19.00
1931	20.00	22.75	18.00 - 19.00
1932	18.00	21.00	18.00 - 19.00
1933	17.50 - 18.00	19.50 - 21.00	17.50 - 19.00

1/ Domestic prices in January were $21 for solid and $27 for flake, as in previous year.
2/ Domestic price of flake in first 2 quarters of 1929 was $25.

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LIST OF PRODUCERS

Establishments Producing Calcium Chloride From Natural Brine (1930)

California Rock Salt Co. (address, 2465 Hunter St., Los Angeles), Saltus, Calif.

J. Q. Dickinson & Co., Malden, W. Va.

Dow Chemical Co., The, Midland, Mich.

Excelsior Salt Works, The, Pomeroy, Ohio.

Liverpool Salt & Coal Co., Hartford, W. Va.

Ohio River Salt Corporation, Mason, W. Va.

Pomeroy Salt Corporation, (address, Pomeroy, Ohio), Minersville, Ohio.

Saline Products (Inc.) (address, 2000 Santa Fe Ave., Los Angeles), Amboy, Calif.

New Texaco Salt Products Co., West Tulsa, Okla.

Establishments Producing Calcium Chloride From Chemical Solvay Process or Other Chemical Waste Liquors (Incomplete List)

Solvay Sales Corporation, Pomeroy, Ohio.

Michigan Alkali Co., 10 E. 40th St., New York, N. Y.

Diamond Alkali Co., Painesville, Ohio.

Columbia Chemical Division of the Pittsburgh Plate Glass Co., Barberton, Ohio.

Ruggles and Rademaker, Manistee, Mich.

Niagara Smelting Corporation, Niagara Falls, N. Y.

Great Western Electrochemical Co., Pittsburgh, Calif.

Carbondale Calcium Co., Carbondale, Pa.

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